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HIGH FIELD SUPERCONDUCTIVITY IN ALKALI METAL INTERCALATES OF MoS_2

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INTRODUCTION

In most applications of superconductors, the properties in high magnetic fields are involved. The most desirable superconductors have high transition temperatures and their superconductivity is not easily quenched by the application of a magnetic field. Most present commercial materials have the cubic β tungsten crystal structure. In the search for better high-temperature, high-critical-field superconductors, a new class of materials has been found which have layered structures and can be intercalated with various elements and compounds.[1] Since a large number of compounds can be formed, intercalation provides a method of control of superconducting properties. They also provide the possible medium for excitonic superconductivity.[2] In this memorandum, we present results of magnetic field studies on alkali metal (Na, K, Rb, and Cs) intercalated MoS_2 (2H polymorph). This study includes: (a) the determination of critical field-temperature boundaries on all compounds; and (b) the superconducting anisotropy in the Cs compound. Zero field studies, an X-ray determination of structure, and stoichiometry, as well as preparation details, were presented earlier.[3]

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EXPERIMENTAL

For magnetic field studies, samples were suspended with layer planes vertical in a glass tube packed with glass wool. Tubes were then mounted in a temperature-controlled dewar in a transverse-field magnet as shown in Fig. 1. The transiton from normal to superconducting states was detected by a self-inductance method,[4] and frequency changes (proportional to susceptibility) were recorded continuously as a function of thermometer resistance on an x-y recorder as shown in Fig. 2. To study the critical temperature as a function of angle between applied field and crystal axes, the apparatus was rotated from above.

RESULTS

Results on $Na_{0.3}MoS_2$ and $K_{0.4}MoS_2$ for magnetic field, H, parallel to layer planes were presented at the 1972 Conference on Layered Compounds (unpublished) and appeared in NASA TM X-68109 (1972).[5] It was found that $Na_{0.3}MoS_2$ had a transition at 4.0 K in zero field with a critical boundary slope dH_c/dT_c of 1.5 tesla/K at 2 tesla. For $K_{0.4}MoS_2$, the zero field transition was at 6.5 K with a slope of 4.2 tesla/K. In this memorandum results are extended to include $Rb_{0.3}MoS_2$ (field in layer planes only), and $Cs_{0.3}MoS_2$ including anisotropy studies. For field in the layer planes, the results are summarized in Fig. 3 where critical field H_c against critical temperature T_c is plotted.

In Fig. 4 the anisotropy for $Cs_{0.3}MoS_2$ is demonstrated in a plot of H_c against T_c for selected angles between H and the layer planes. The original data were taken by varying T at fixed θ for a series of H values and taken again by varying T at fixed H for a series of closely spaced angles. Figure 4 represents the best fit to all the $Cs_{0.3}MoS_2$ anisotropy data on sample no. 1 (JPL no. RS30IC-PPA).

DISCUSSION

In table I the zero field transition temperatures and the slopes of the H_c against T_c boundaries for H in the layer planes are shown for easy comparison. These transition temperatures are relatively high compared with intercalated compounds studied so far. Critical boundary slopes are steep compared with superconductors having the β tungsten crystal structure (e.g., Nb_3Sn), and are comparable to those found in $NbSe_2$,[6] also a layered compound. Critical current densities, J_c, would also be of interest, but very few J_c studies have been done on layered compounds.[7]

An interesting trend is seen in table I. The slope of the critical field-temperature boundary scales roughly with the c-axis expansion and inversely with ionization potential (with one exception). The scaling of critical boundary with c-axis expansion is opposite to the effect found by Foner in other compounds.[6]

An essential unanswered question in layered compounds, especially intercalated compounds, is whether superconductivity is two dimensional (confined to each MoS_2 layer) or if Cooper pairing occurs across layers. Help in answering these questions can come from a study of the high field anisotropy. We have taken two approaches to analysis: (1) to consider the anisotropy found in thin films, and the high field theory for films; (2) to compare results with theories which account for pairing across layer planes.

In thin (noncrystalline[8]) films, superconducting transition temperatures increase inversely with thickness d (to some power). It is also well known that H_c values are elevated for H applied in the film plane, due to surface nucleation[9] of superconductivity. Thus $H_c \simeq 1.7\, H_{c2}$, where H_{c2} is the bulk critical field for a type II superconductor. (H_c means H parallel to layer planes.)

For the general thin film case, Tinkham[10] finds

$$\left(\frac{H_c(\theta)}{H_{c_{\parallel}}}\cos\theta\right)^2 + \frac{H_c(\theta)}{H_{c_{\perp}}}\sin\theta = 1 \qquad (1)$$

for $d \ll \xi$ where d is film thickness, ξ is coherence length, $H_c(\theta)$ is the critical field at angle θ between H and the plane of the film. Solving (1) for $\sin\theta$ yields

$$\sin\theta = \frac{\dfrac{H_c(\theta)}{H_{c_{\perp}}} - \sqrt{\left(\dfrac{H_c(\theta)}{H_{c_{\perp}}}\right)^2 - 4\left(\dfrac{H_c(\theta)}{H_{c_{\parallel}}}\right)^2\left[1 - \left(\dfrac{H_c(\theta)}{H_{c_{\perp}}}\right)^2\right]}}{2\left(\dfrac{H_c(\theta)}{H_{c_{\parallel}}}\right)^2} \equiv F(\theta, H) \qquad (2)$$

In Fig. 5 we plot the function $\sin\theta$ and the righthand side $(F(\theta, H)$ of Eq. (2) calculated from our data. It is seen that our data on $Cs_{0.3}MoS_2$ does not fit relations (1) and (2) at 5.8 Kelvins. One might expect a fit if superconductivity were confined to the MoS_2 layers with no pairing across layers

For the case of coupling across planes, Katz,[11] and Morris, et al.[12] find

$$\left(\frac{H_c(\theta)}{H_{c_{\perp}}}\right)^2 = (\sin^2\theta + \epsilon^2\cos^2\theta)^{-1} \qquad (3)$$

where $\epsilon^2 = m/M$ and m and M are effective masses for parallel and perpendicular orientations. A plot of Eq. (3) and experimental data for $Cs_{0.3}MoS_2$ (normalized for field parallel and perpendicular data) is shown in Fig. 6 for the lowest temperature (5.8 K) considered at the time of writing. The agreement is not good. However, a plot of the difference between the experimental and calculated curves against temperature show a rapid trend towards a fit to (2) at lower temperatures. Definite conclusions will have to await higher field and lower temperature data. From Fig. 6 and Eq. (2), $\epsilon^2 = m/M \simeq 1/48$, at 5.8 K. Following Morris, et al,[12] this demonstrates an anisotropy of the superconducting coherence length (between parallel and perpendicular orientations) of seven to one for the $Cs_{0.3}MoS_2$ compound at 5.8 K.

We would finally like to point out a very unusual result: We have found a <u>positive</u> curvature $(\partial^2 H_c/\partial T_c^2)$ in the H_c against T_c phase plane for all samples at fields below one tesla (as shown in fig. 4 for $Cs_{0.3}MoS_2$). (See ref. 5 also.) We have found no theoretical explanation for this. It is not likely to be due to the ~100 kHz frequency of our self inductance circuit since it appears in data taken using a mutual inductance method at 17 Hz.

REFERENCES

1. F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, Science <u>174</u>, 493 (1971).

2. See: J. A. Wilson and A. D. Yoffe, Adv. Phys. <u>18</u>, 280 (1969), and references to Ginsburg therein.

3. R. B. Somoano, V. Hadek, and A. Rembaum, "The Alkali Metal Intercalates of Molybdenum Disulfide," accepted for publication in J. Chem. Phys., 1973.

4. A. L. Schawlow and G. E. Devlin, Phys. Rev. <u>113</u>, 120 (1959).

5. J. A. Woollam, D. J. Flood, D. E. Wagoner, R. E. Somoano, and A. Rembaum, NASA TM X-68109 (1972).

6. S. Foner, Conference on the Physics and Chemistry of Layered Compounds and Their Intercalate (unpublished), Monterey, Calif. (Aug. 1972).

7. E. A. Antonova, S. A. Medvedev, and I. Yu. Shebalin, Sov. Phys. JETP 30, 181 (1970).

8. M. Strongin, O. F. Kammerer, H. H. Farrell, and D. L. Miller, Phys. Rev. Letters 30, 129 (1973).

9. W. J. Tomash and A. S. Joseph, Phys. Rev. Letters 12, 148 (1964).

10. M. Tinkham, Phys. Rev. 129, 2413 (1963).

11. E. I. Katz, Sov. Phys. JETP, 31, 787 (1970).

12. R. C. Morris, R. V. Coleman, and R. Bhandari, Phys. Rev. B5, 895 (1972).

TABLE I

Compound	T_c (H = 0), K	$\frac{dHc}{dT}$ (at 2 tesla), T/K	ΔC_0, 10^{-10}m over MoS_2	Ionization potential	Ionic radii, 10^{-10}m
$Na_{0.3}MoS_2$	4.0	1.5	2.7	5.12	0.98
$K_{0.4}MoS_2$	6.5	4.2	4.29	4.32	1.33
$Rb_{0.3}MoS_2$	[a]6.5 to 7.0	[a]2.4 to 2.7	4.90	4.16	1.48
$Cs_{0.3}MoS_2$	[a]6.75 to 7.1	6.0	7.31	3.87	1.67

[a]Depending on particular sample.

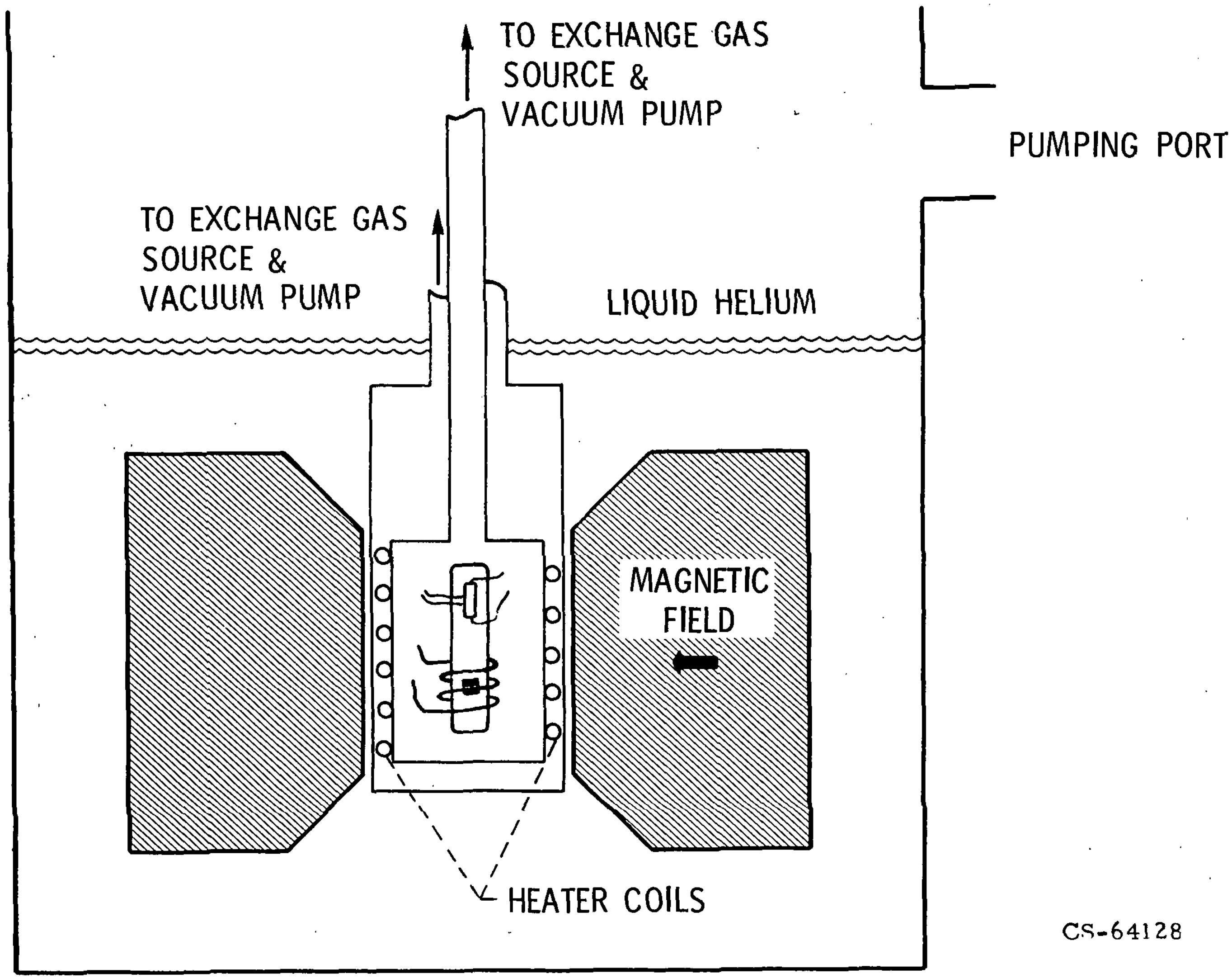

Figure 1. - Cryostat and double vacuum/exchange gas system.

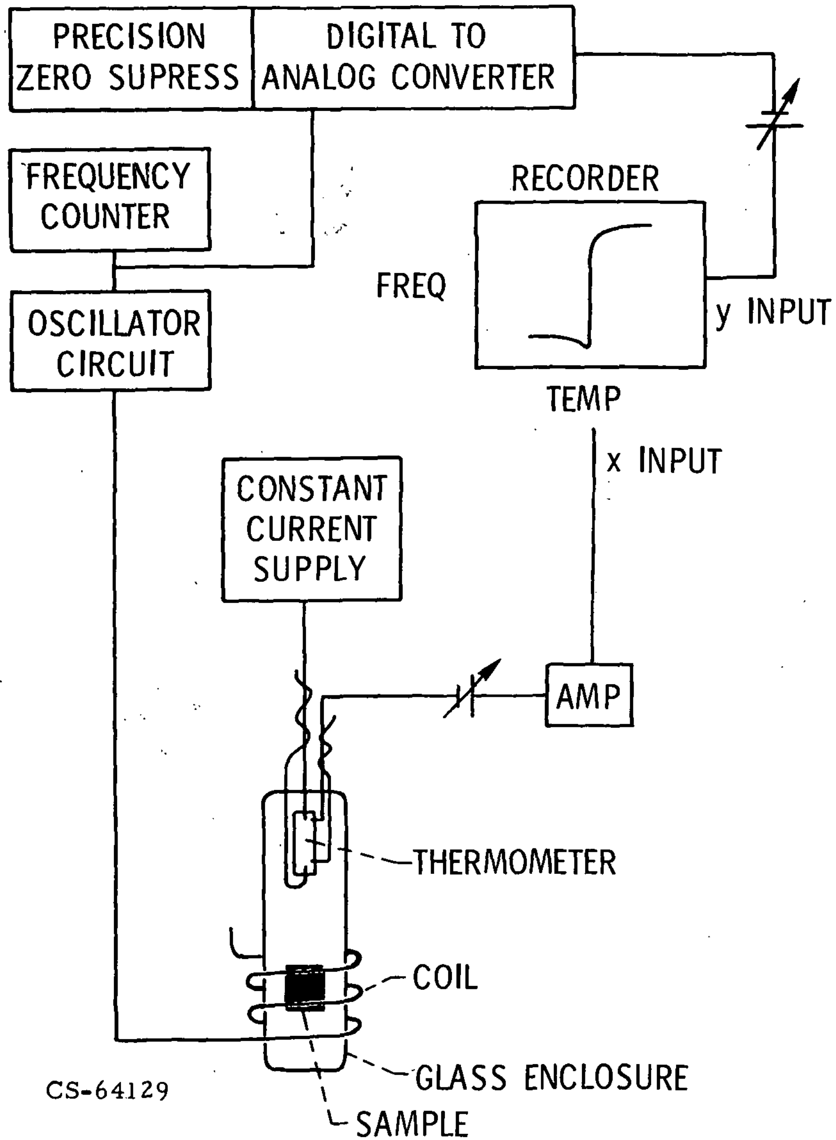

Figure 2. - Basic circuitry for superconducting transition studies.

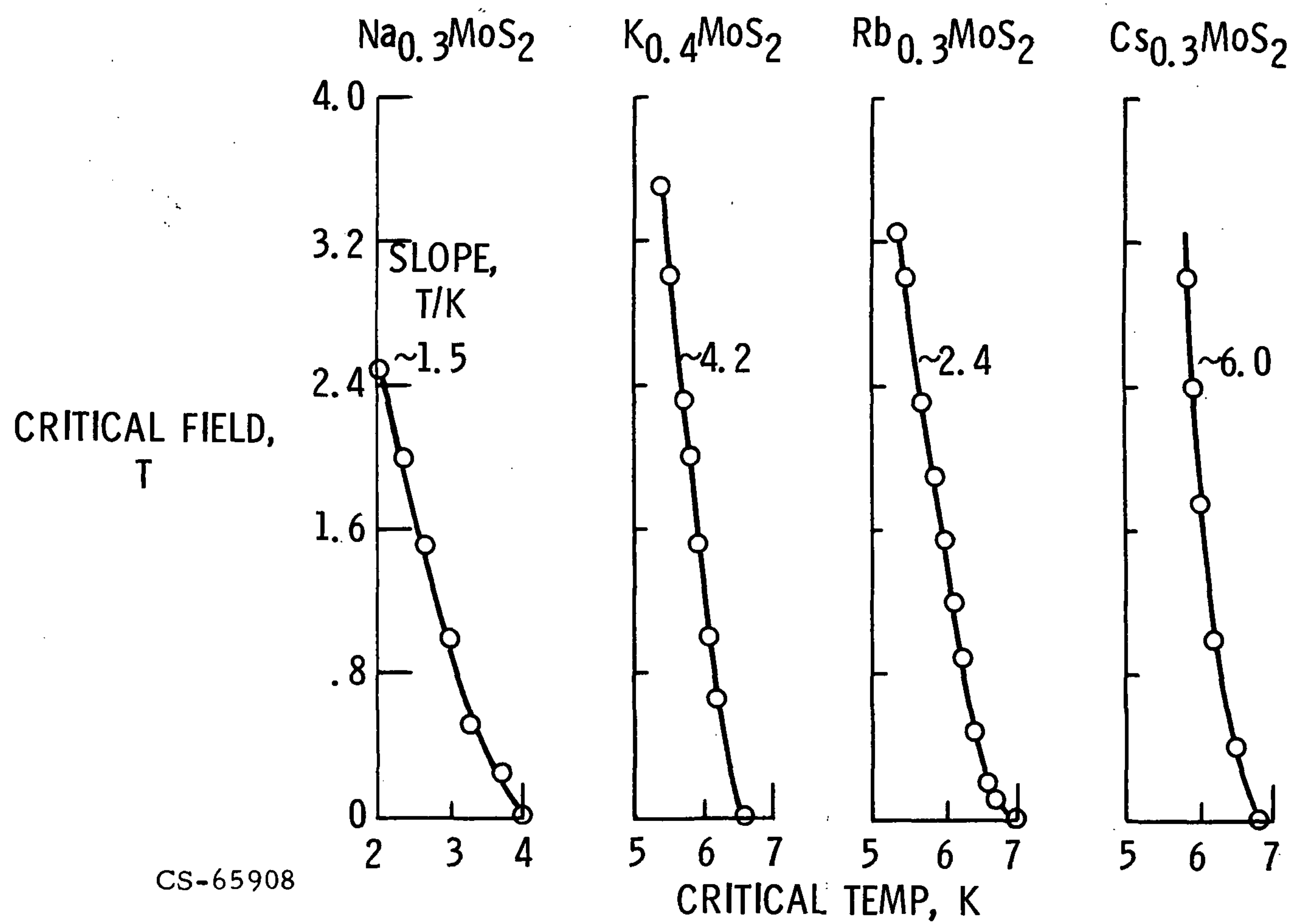

Figure 3. - Composite of critical field vs critical temperature data for field parallel to layer planes for Na, K, Rb, and Cs compounds.

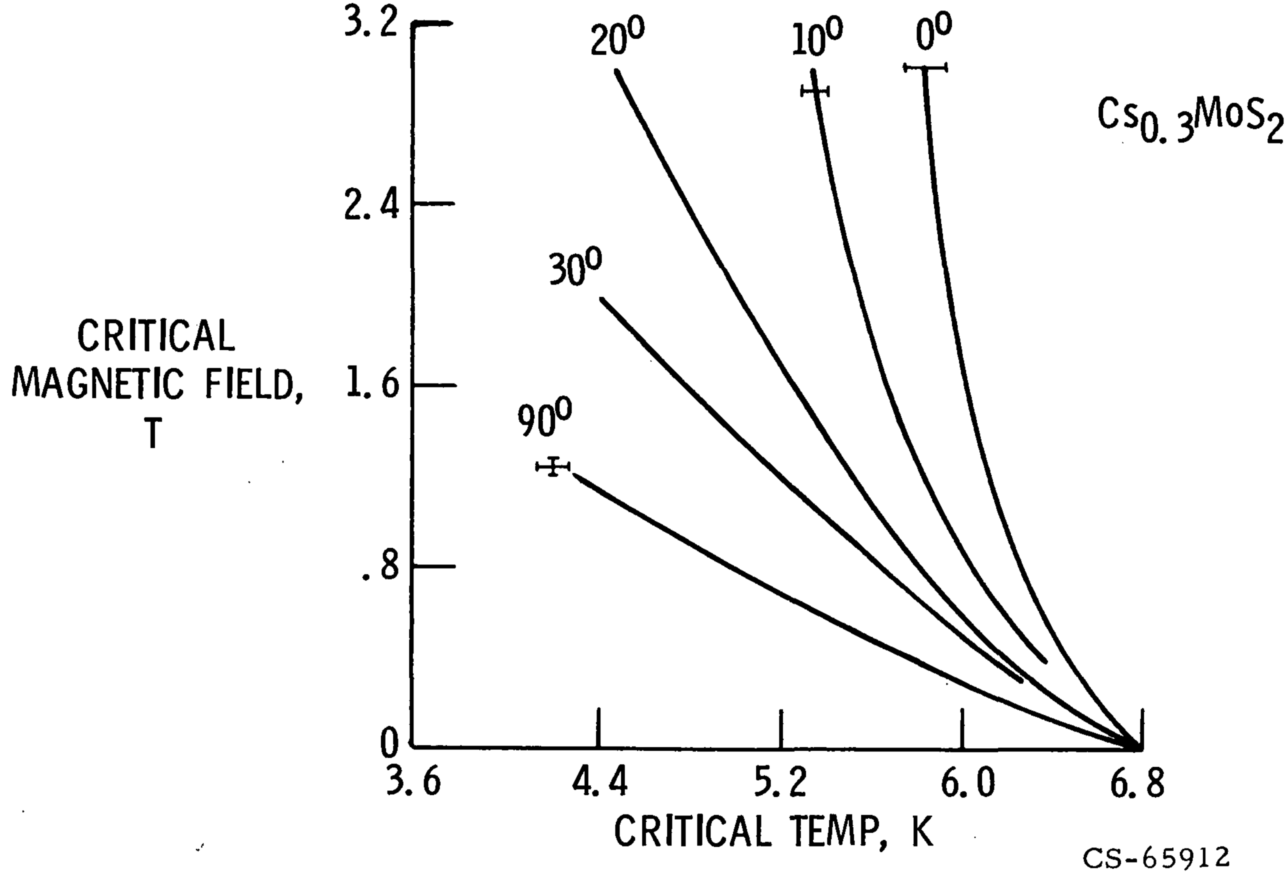

Figure 4. - Critical field vs critical temperature for a $Cs_{0.3}MoS_2$ compound for various angles between the layer planes and the applied magnetic field. SAMPLE NO. 1

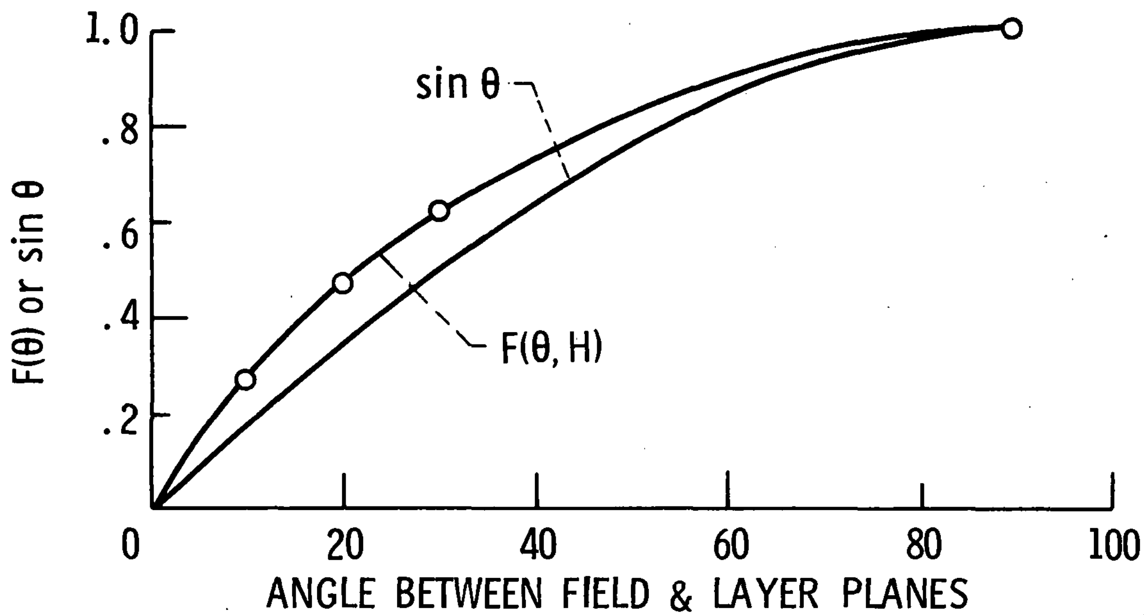

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Figure 5. - A plot of two functions, sin θ, and equation (2), vs angle between applied field and layer planes for $Cs_{0.3}MoS_2$ at 5.8 K. SAMPLE NO. 1

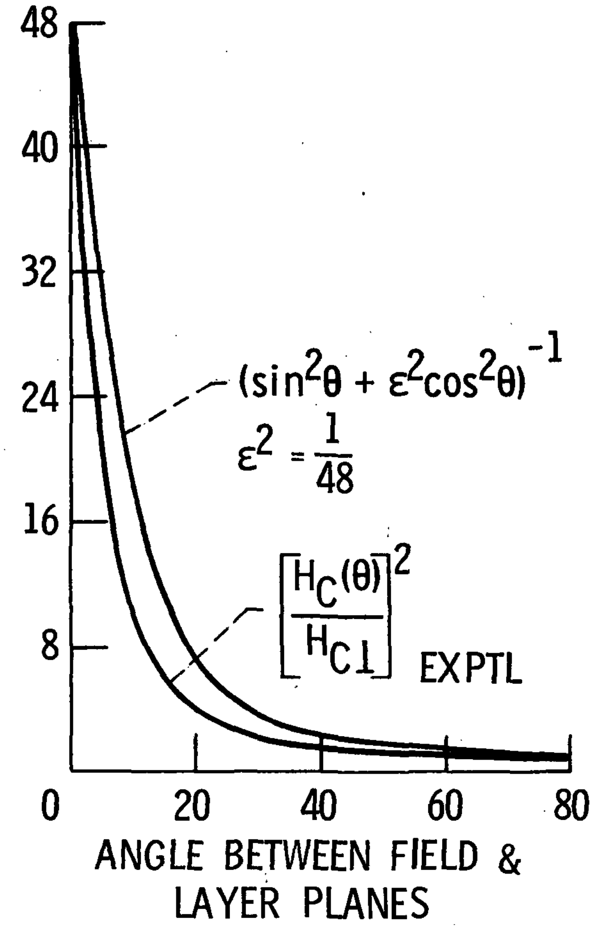

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Figure 6. - A plot of the two sides of equation (3) vs angle between applied field and layer planes for $Cs_{0.3}MoS_2$ at 5.8 K. SAMPLE NO. 1